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Wesley R. Cofer III

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Enhanced Hydrophilicity of Chlorided Aluminum Oxide Particulates

Wesley R. Cofer III
Langley Research Center
Hampton, Virginia



National Aeronautics
and Space Administration

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SUMMARY

An enhancement of hydrophilicity for chlorided aluminas has been demonstrated by the results obtained from gaseous H_2O sorptions at 70-, 80-, and 86-percent relative humidity on alpha and gamma aluminum oxide particulates and on alpha and gamma aluminum oxide particulates with a chemisorbed surface chloride phase (produced by reactions of gaseous $\text{HCl} + \text{H}_2\text{O}$ on alumina). Continuous sorption histories for H_2O on chlorided aluminas having specific surface areas that range from 7 to $227 \text{ m}^2/\text{g}$ before chloriding indicated that initial sorption rates were directly linked to the extent of chemisorbed chlorided coverage and implied the same relationship for sorption capacities. The initial sorption rate on chlorided aluminas was found to be slower for the first exposure to H_2O than for subsequent exposures (which reached equilibrated H_2O coverages much faster), suggesting that "slow" chemical reactions between H_2O and chlorided alumina may have been operative during initial exposures. Chlorided alumina particles were found to remain very hydrophilic (relative to nonchlorided analogs) for several H_2O sorption/desorption cycles.

These results should point out the need for a better understanding of the nature of solid-propellant rocket-motor exhaust alumina (in particular, surface properties) since many long term (several days) environmental impacts may be significantly influenced by surface characteristics.

INTRODUCTION

Hydrogen chloride (HCl) and aluminum oxide (Al_2O_3) are primary exhaust products of ammonium perchlorate based solid-propellant rocket motors (SRM). The impact of these exhaust products on the environment, particularly in the quantities calculated to be released by the Space Shuttle boosters (ref. 1), is of concern to the National Aeronautics and Space Administration. Currently, time-dependent analytical models are used to predict atmospheric dispersion and speciation of SRM exhaust products. These models rely, in part, on chemical input parameters to predict environmental impacts. Consequently, the behavior of potentially reactive chemical systems such as HCl and Al_2O_3 in the presence of H_2O is essential to accurate model predictions.

Previous work (ref. 2) characterized the sorptions of gaseous $\text{HCl}/\text{H}_2\text{O}$ mixtures in nitrogen (N_2) on samples of calcination-produced alumina at room temperatures and pressures (RTP). The results indicated that H_2O soluble aluminum salts (chlorides and/or oxychlorides) were formed on the surface of the alumina as the result of gas-solid $\text{H}_2\text{O}/\text{HCl}/\text{Al}_2\text{O}_3$ reactions. Steady-state chemisorbed coverages of $\text{H}_2\text{O} + \text{HCl}$ ($\approx 1 \text{ mg}/\text{m}^2$) were observed in quantities which were considered sufficient to alter the surface properties of both gamma and alpha alumina particles.

Since these crystalline phases have been identified in SRM exhaust (refs. 3 and 4) and since a reasonable likelihood exists that these phases

will become "chlorided" (refs. 2 and 4), a study was undertaken to contrast the hydrophilic behavior of chlorided alumina particulates with equivalent nonchlorided particles. This work will focus on the sorption behavior of H₂O on chlorided alumina and is viewed as a logical extension of the previous study which characterizes the simultaneous sorptions of HCl + H₂O mixtures on "pure" alumina. In an aged SRM exhaust (i.e., when gaseous HCl concentrations have been greatly reduced through atmospheric dilution), atmospheric H₂O interactions with particulate alumina may be significantly altered by surface chloride coverages. Nucleation mechanisms, as well as condensation and growth processes in atmospheric SRM aerosols, may ultimately be largely influenced by the character and composition of the particulate surface. Water sorption on chlorided alumina, therefore, should be of particular interest to those concerned with inadvertent weather modification resulting from large amounts of SRM exhaust.

EXPERIMENTAL

A gravimetric sorption technique was used for this study. An electrobalance fitted with both digital and strip-chart-recorder readout was used to continuously record weight gains (or losses) during sample sorption/desorption histories. A schematic of the experimental system is shown in figure 1. All sorptions were conducted at room temperature (maintained between 22° and 25° C) and ambient laboratory pressures. The background noise level for the microbalance system was determined to be ±3 mg.

Alumina Preparation

The preparation and characterization of aluminas used in these experiments are covered in detail in the HCl/H₂O sorption studies (ref. 2). A brief summary of the aluminas used in this report appears in table I.

TABLE I.- CHARACTERIZATION OF ALUMINAS

Preparation	Crystalline phase	Calcination temperature, °C	Surface area (N ₂ BET), m ² /g
3	Gamma	700	92.9
6	Gamma	625	142.0
7	Alpha	1025	7.1
9	Gamma	600	226.9

Alumina preparations were analyzed by X-ray diffractometry to confirm crystalline variety, and BET surface areas were determined by low-temperature N₂

adsorption (work by R. R. Bailey and J. P. Wightman at Virginia Polytechnic Institute and State University).

Sample Preparation

Alumina particulates were dispersed in a closed vessel by using a blast of dry nitrogen and were allowed to settle uniformly over a 12-mm-diameter platinum pan, which was then quickly placed in the 1.1 l exposure chamber and desorbed into a continuous flow (300 cm³/min) of high-purity nitrogen. The chamber and associated supporting apparatus were pyrex. All samples tested had an initial weight of approximately 1 mg, except those from preparation 7 for which larger (~3 mg) samples were desirable because they produced weight gains that were easier to accurately measure. After 3 to 4 hours of desorption into dry nitrogen, which produces a reproducible initial reference state, sample preparation was complete. At this point, the prepared nonchlorided sample was exposed to the appropriate gas mixtures for the sorption/desorption histograms.

Chloriding Pretreatment

Samples of alumina were prepared as previously described and then exposed to gaseous H₂O/HCl/N₂ mixtures that were generated by passing 150 cm³/min (all flow rates stated in standard cm³/min) of N₂ through a "source bubbler" containing 6-molar hydrochloric acid. An additional 50 cm³/min of dry N₂ was fed through the balance head into the exposure chamber to prevent diffusion of HCl into the balance electronics. The output concentration of HCl was experimentally measured in previous experiments (ref. 2), and steady-state chamber concentrations for HCl and H₂O were calculated to be 300 and 17 500 ppm, respectively. Since each alumina preparation was demonstrated (ref. 2) to have a definite maximum surface chloriding capacity, samples were either (1) allowed to reach steady-state coverage and then desorbed into N₂ to produce a saturated chloride coverage or (2) were desorbed before reaching steady state to produce a fractional chemisorbed chloride coverage. Chlorided samples in this text will be referred to as either fully chlorided or as some percent chlorided. This completed the prechloriding treatment, and samples were then exposed to gaseous H₂O/N₂ mixtures for subsequent hydrophilicity information. Reference weights (W₀ given in mg), from which percent weight gains were computed for subsequent H₂O exposures, are presented for each run in the appropriate figures.

Water Vapor Mixtures

Gaseous mixtures of water vapor in nitrogen were generated by first passing 150 cm³/min of N₂ through the source bubbler which contained distilled water instead of hydrochloric acid and by then feeding the effluent into the exposure chamber. Flows (15, 25, or 50 cm³/min) of additional dry N₂ diluent were added to the primary source output through the balance head (fig. 1) and were assumed to mix thoroughly in the exposure chamber. This furnished a method for adjusting chamber humidities while protecting vital balance electronics from excessive moisture or from HCl in the prechloriding treatment.

Humidity measurements were made at the exit port of the exposure chamber (fig. 1) with a dewpoint hygrometer that was equipped with an aluminum oxide sensor probe. Response time was given as less than 5 sec for a 63-percent change in moisture for this probe. Time-dependent relative-humidity (R.H.) curves for the chamber with 15, 25, and 50 cm³/min diluent flows of N₂ are shown in figure 2. Steady-state humidities are apparently reached in about 3 hr (180 min) for all cases. The curve thickness represents the spread in relative humidity that is obtained from three individual runs at each prescribed diluent flow rate. Arithmetic mean steady-state humidities for the 15, 25, and 50 cm³/min diluent flows were determined to be 86, 80, and 70, respectively. Relative-humidity readings were not taken during sample exposure runs since even trace quantities of gaseous HCl were considered potentially destructive to the sensor probe. Humidity measurements were made with an unloaded weighing pan while all other parameters were held identical to actual exposure conditions. For convenience and simplicity, the equilibrated chamber humidities for runs using 15, 25, or 50 cm³/min of N₂ diluent will be referred to as 86-, 80-, and 70-percent saturations, respectively, even though ± 3 -percent deviations in relative humidity should be expected among individual runs.

Corrections for H₂O adsorption on the empty weighing pan and supporting apparatus were insignificant except with low-surface area preparation 7 alumina which gained very little weight and during initial exposure times (<60 min) on the remaining batches.

Multiple Exposures

Multiple water exposure cycles were conducted on alumina samples as follows: Chlorided (or nonchlorided) samples were initially exposed to water vapor as previously described and then desorbed into dry nitrogen until no measurable weight loss resulted (typically 3 hr (180 min)). Samples were then reexposed to a second water sorption/desorption cycle. This procedure was repeated for as many cycles as were desired. The reference weight for each successive exposure was the weight retained from the prior cycle.

RESULTS AND DISCUSSION

First Exposures

The sorption behavior for 12 individual, nonchlorided alumina samples exposed to water vapor at 70-, 80-, and 86-percent relative humidity is shown in figures 3 to 6. All four alumina preparations used for this study are represented in these figures. As expected, equilibrated weight gains can be seen to increase with increasing exposure humidity. Rates of weight gain appear initially higher for higher exposure humidities. Equilibrated H₂O coverages for these preparations at their respective humidities are given in table II.

TABLE II.- STEADY-STATE WATER COVERAGES ON NONCHLORIDED ALUMINAS

Preparation	Crystalline phase	Surface coverage for 70-percent R.H., mg/m ²	Surface coverage for 80-percent R.H., mg/m ²	Surface coverage for 86-percent R.H., mg/m ²
3	Gamma	0.56	0.80	1.26
6	Gamma	.65	.99	1.24
7	Alpha	.65	.83	.94
9	Gamma	.76	.87	.99

Although the overall trend toward higher coverages at higher humidities is evident in table II, specific sorptions among the individual preparations appear to vary randomly at the different relative humidities. No attempt will be made to explain this variance.

The sorptions of three fully chlorided samples of preparation 9 alumina are shown in figure 7 at 70-, 80-, and 86-percent relative humidity. Water coverage at each humidity appears significantly increased on these fully chlorided samples when compared with nonchlorided counterparts (fig. 6) at equivalent times. No tendency for these fully chlorided samples to reach steady-state coverage is discernible.

Figure 8 shows the sorption behavior of H₂O at 70-percent relative humidity on three different samples (fully chlorided, 76-percent chlorided, and 55-percent chlorided) of preparation 9 alumina. These results indicate an increasing rate of water sorption (and suggest an increased capacity) coupled to the extent of chemisorbed chloride coverage for time $t \leq 20$ hr (1200 min). Steady-state H₂O coverages would be anticipated to increase with increasing surface chloride content if it is assumed that a hygroscopic aluminum chloride/oxychloride salt results from the chloriding procedure.

Data from the above runs, as well as additional data at 86-percent relative humidity, are plotted in figures 9 and 10 to further emphasize the relationship between relative hydrophilicity and the extent of chloride coverage at several designated times.

Steady-state water coverages were not determined for most chlorided samples of alumina since weight gains usually extended well beyond the time frames considered applicable to atmospheric SRM interactions. That is, relatively constant humidities would not be anticipated in actual SRM clouds for such extended periods. A further example of this is shown in figure 11, where weight gain is depicted extending to 100 hr (6000 min) on preparation 6 alumina that is exposed to water at 86-percent relative humidity.

The sorption histories of H₂O at 70-percent relative humidity on a fully chlorided and a nonchlorided sample of alpha alumina are shown in figure 12. The result of prechloriding is apparent. Surface coverages (near equilibrium) of water have increased by a factor of 3.5. It is worth noting that nonchlorided samples typically reach steady-state H₂O coverages within several hours although chlorided samples more frequently require much longer periods of time. In fact, samples of preparation 7 alumina were the only chlorided samples reaching steady state within 20 hr (1200 min) of a first water exposure.

More typical behavior for the higher surface area aluminas is shown in figure 13 where a 65-percent prechlorided sample of preparation 3 alumina required approximately 50 hr (3000 min) to reach steady-state H₂O coverage at 86-percent relative humidity. Since most runs were terminated after 20 hr (1200 min), little data were taken that could be used to characterize steady-state H₂O coverages during the first exposure.

Multiple Exposures

Since individual particulates in an atmospheric aerosol may experience highly variable relative humidities during the history of the aerosol, experiments were conducted to determine whether significant changes in the sorption characteristics for H₂O on chlorided alumina would result from multiple sorption/desorption cycles. Although the relative humidities that were reached after desorption into N₂ for these experiments would not be expected in atmospheric aerosols, "zero" humidity was experimentally desirable since it furnished a well-defined stationary reference point and allowed the comparison of complete sorption histories among all runs. The results of one such experiment are shown in figures 14 and 15. The prechloriding history is included in figure 14, and after desorption into dry N₂, a 23-percent chemisorbed weight gain (92 percent of saturated coverage) resulted. The valving was then changed and the sample exposed to its first H₂O cycle at 70-percent relative humidity. The sample was desorbed into N₂ and reexposed to water vapor at 80-percent relative humidity. The process was repeated for six cycles (labeled in figs. 14 and 15) at the noted humidities and involved over 115 hr (6900 min) of exposures. It is significant that these chlorided samples retained their hydrophilic nature relative to their nonchlorided counterparts for many cycles involving many hours. Additional evidence supporting the retention of hydrophilic character after multiple sorption/desorption cycles is presented in figure 16, where a fully chlorided sample of preparation 3 alumina was exposed to three water cycles. The second exposure can clearly be seen to produce a more rapid weight gain than the first. Samples exposed to multiple H₂O cycling appeared to reach steady-state weight gains more rapidly than their singularly exposed counterparts and displayed higher initial sorption rates. This can be seen by comparing figures 14 and 15 with figures 8 and 10 (for preparation 9 alumina) and figure 13 with figure 16 (for preparation 3 alumina). Steady-state water coverages were reached in time frames progressively approaching those observed with the nonchlorided samples. (See figs. 3 and 6.)

Steady-state H₂O coverages for these data are listed in table III.

TABLE III.- STEADY-STATE H₂O COVERAGES

Relative humidity, percent	Surface coverage, mg/m ² , for preparation -	
	9	3
70	1.5	---
80	2.6	---
86	4.4	4.7

It seems reasonable to suggest that "slow" chemical reactions of H₂O with chlorided aluminas are responsible for the differences between successive water exposures. Since it has been suggested (ref. 2) that aluminum chlorides and oxychlorides form on the surface of alumina exposed to gaseous HCl + H₂O mixtures and that speciation is potentially linked to acidity, slow conversion of chlorides to oxychlorides or oxychlorides to "higher oxychlorides" in a less acidic environment (particles equilibrating with H₂O rather than H₂O + HCl mixtures) would not be improbable. By careful examination of figures 14, 15, and 16, most of the reactions can be deduced to occur primarily during the first H₂O exposure cycle. That is, in figures 14 and 15, the second and fifth H₂O cycles at 80-percent relative humidity are very similar in curve shape while the third and sixth exposures are nearly equivalent. The sorption curves for the first and fourth sorptions, however, are significantly different. The general shape of the sorption curves for first and second exposures at 80-percent relative humidity on preparation 3 alumina (fig. 16) tends to verify the results observed in figures 14 and 15. Early sorption is apparently retarded during the first exposure.

The first and second sorptions of H₂O at 70-percent relative humidity on a nonchlorided sample of preparation 3 alumina are shown in figure 17. Here, as with the chlorided samples, the second sorption appears initially accelerated. This observation would have been somewhat unexpected if chemisorption of H₂O on nonchlorided aluminas (ref. 3) had not been previously demonstrated (i.e., H₂O coverages (≈ 0.1 mg/m²) typically about one-tenth that of the chemisorbed coverages resulting from HCl + H₂O exposures). Again, slow chemical reactions between alumina and H₂O (e.g., hydrations) are suggested as an explanation of this sorption phenomena.

CONCLUDING REMARKS

Experimental results have demonstrated that aluminum oxide particulates with a chemisorbed surface chloride phase are more hydrophilic than their nonchlorided counterparts. Results have been presented that indicate the sorption

rate for water on the particulates is linked to the extent of chloriding and imply the same relationship for sorption capacities. Although water sorptions on nonchlorided samples at given humidities generally equilibrated within several hours, chlorided alumina, when first exposed to water vapor, rarely equilibrated within typical exposure times (24 hr (1440 min)). Slow chemical reactions of sorbed water with chlorided alumina have been suggested to explain this behavior. When chlorided alumina samples were exposed to several H₂O sorption/desorption cycles (\approx 20 hr/cycle), however, equilibration times progressively approached those observed on nonchlorided samples. Usually by the third exposure, equilibration times had become nearly identical and suggest the diminishing importance of H₂O reactions. Relative to nonchlorided samples, however, chlorided samples still remained very hydrophilic for as many as six H₂O cycles involving over 115 hr (6900 min) of exposures.

It is hoped that this work has demonstrated that chlorided SRM exhaust alumina could interact differently with atmospheric H₂O than its nonchlorided analog. Therefore, the use of data derived from "pure" alumina particulates may be inadequate for predicting H₂O-particle interactions in solid-propellant rocket motor (SRM) exhaust aerosols. Although these results are not complete enough to integrate into a quantitative scheme predicting SRM aerosol behavior, the need for better characterization of the surface properties of SRM exhaust alumina has been demonstrated.

Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23665
September 15, 1978

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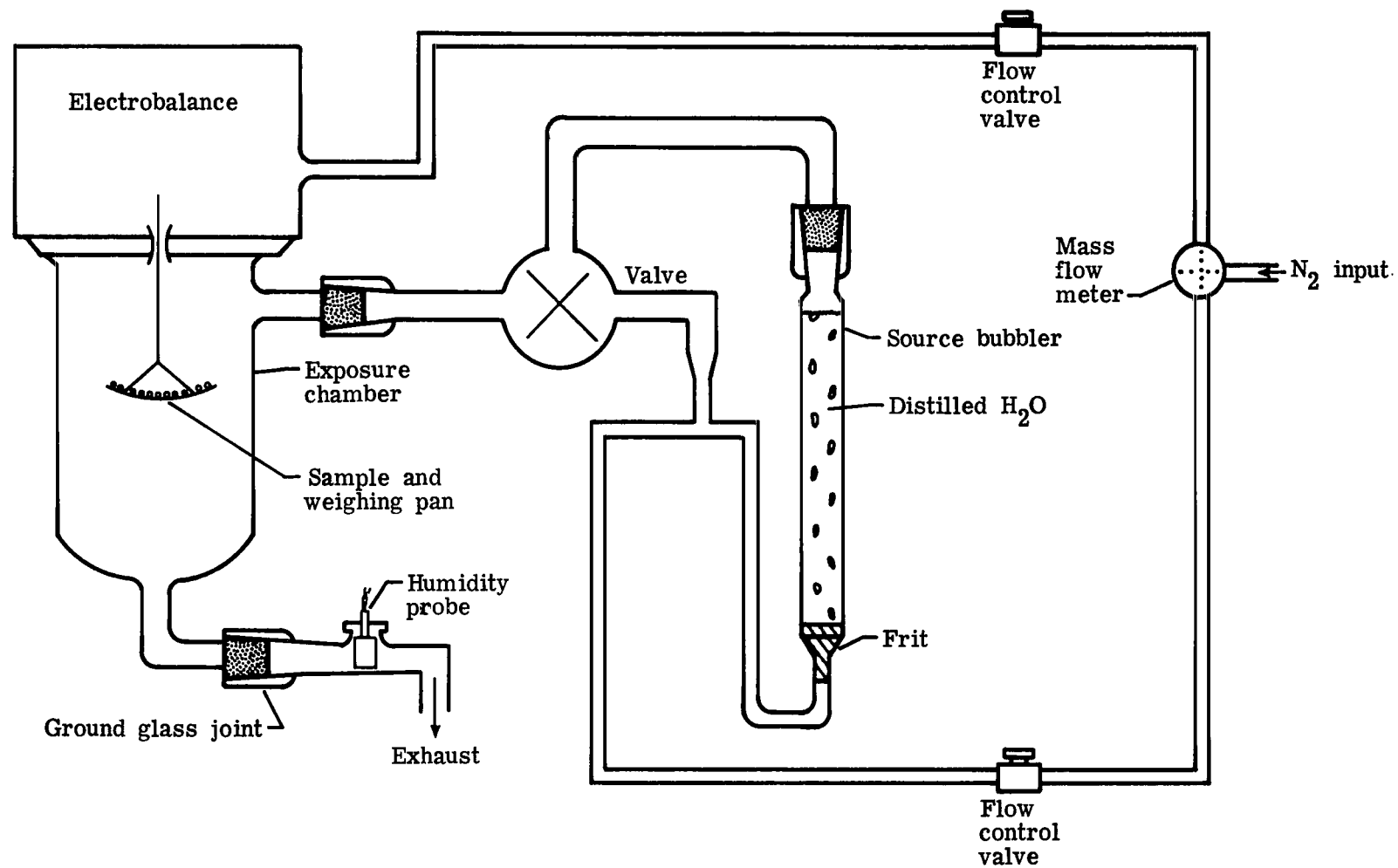


Figure 1.- Experimental apparatus for H₂O sorption measurements.

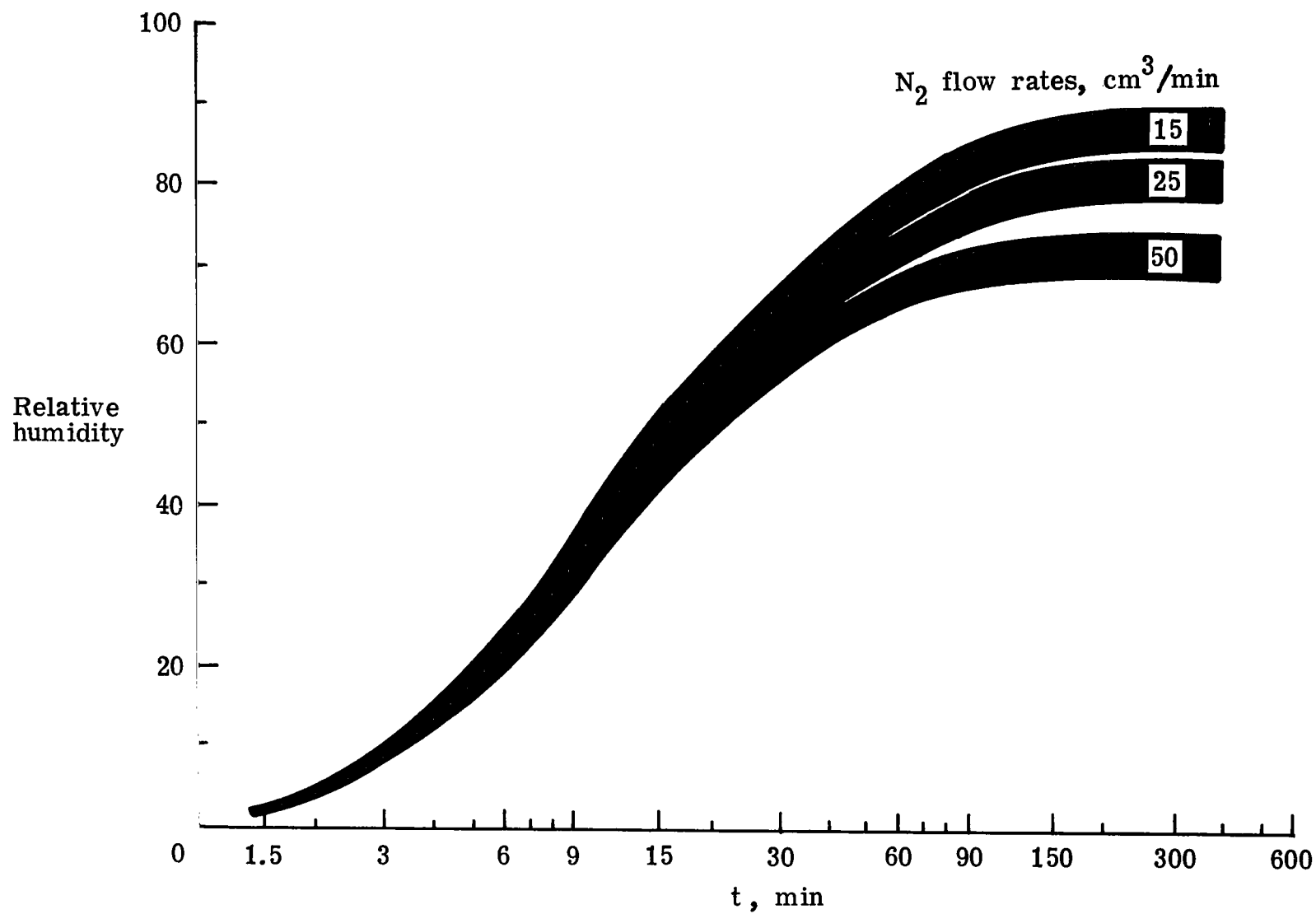


Figure 2.- Relative humidities in exposure chamber at preset N₂ diluent flows as a function of time.

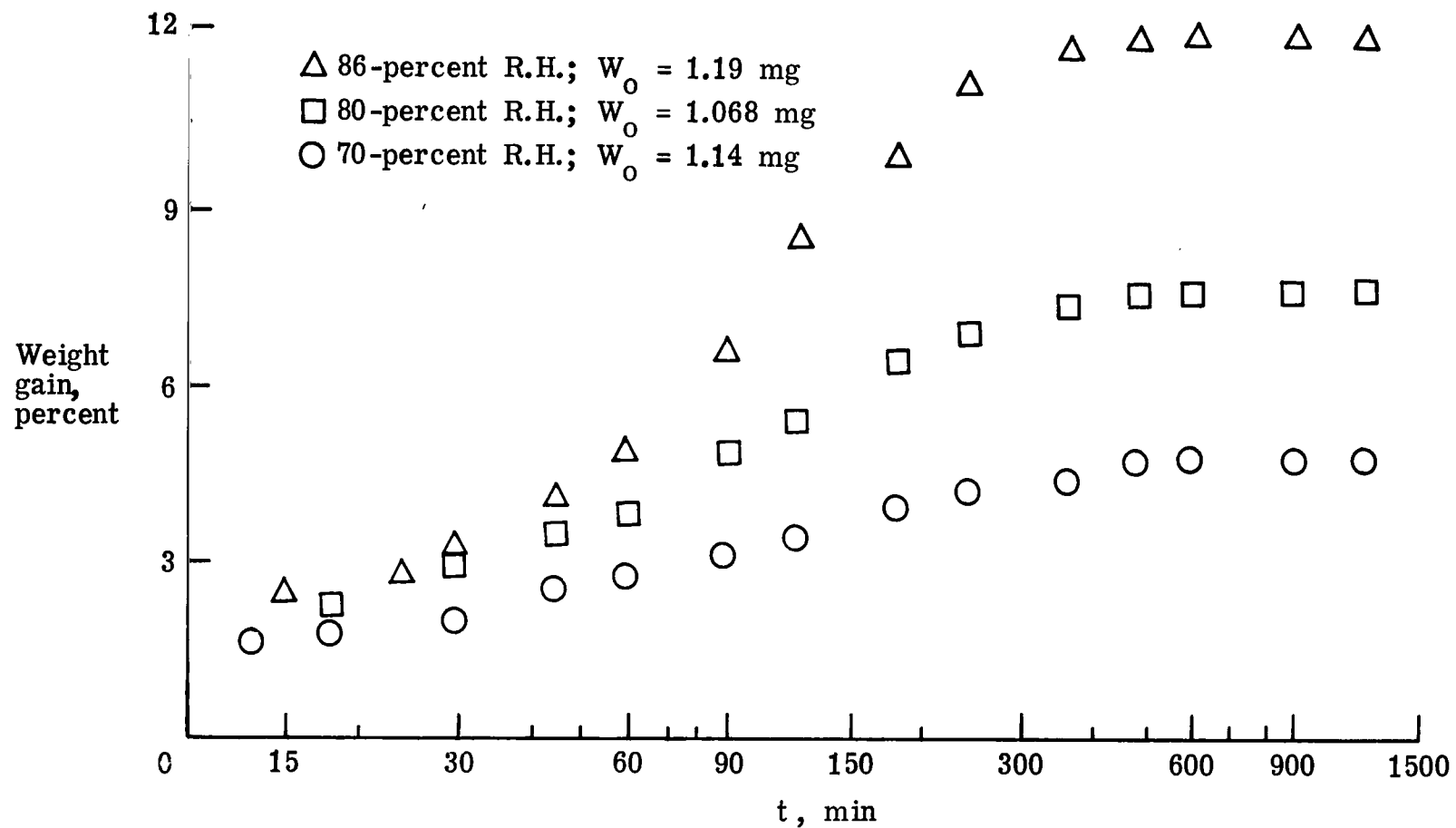


Figure 3.- Water sorption on samples of preparation 3 alumina without prechloriding exposure.

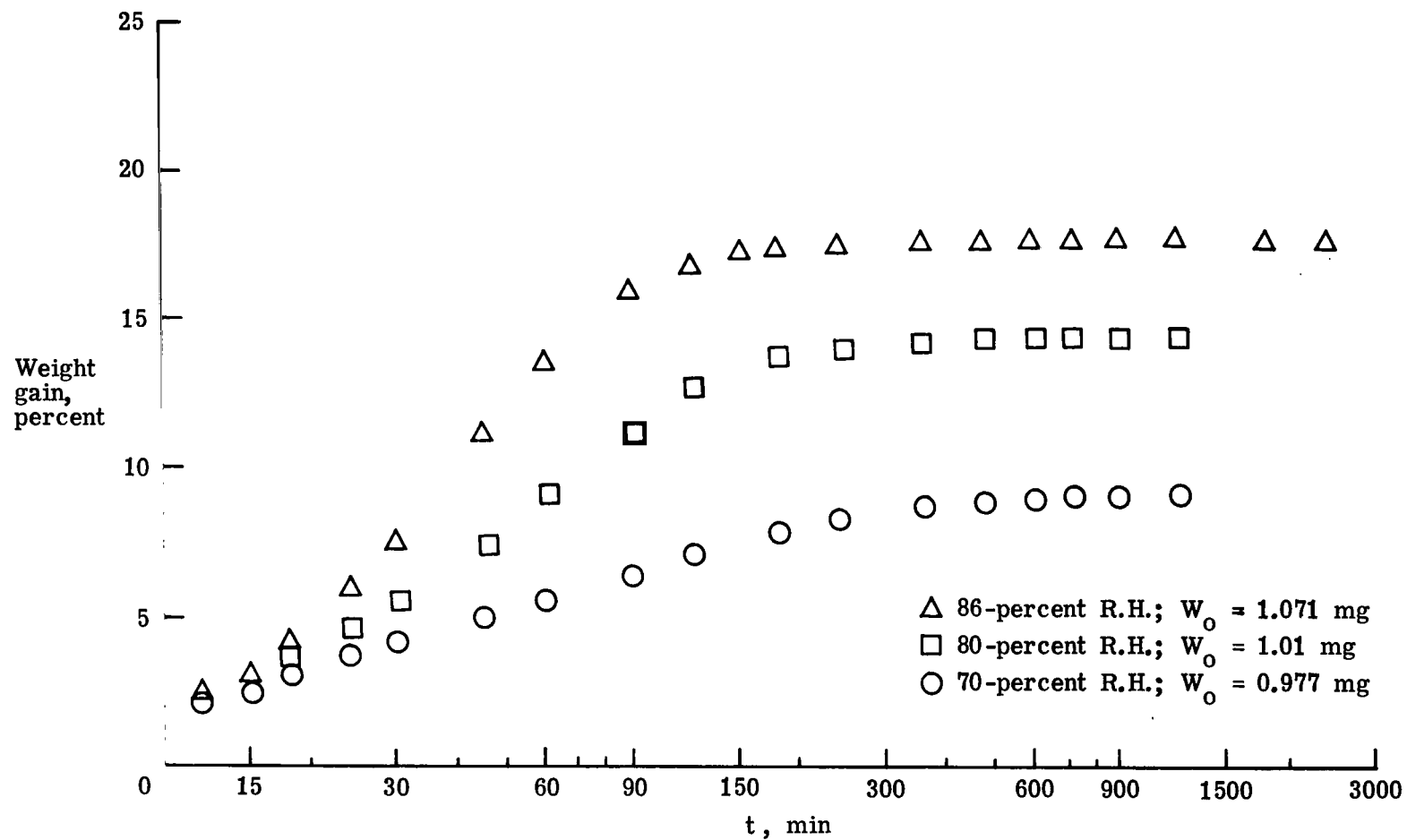


Figure 4.- Water sorption on samples of preparation 6 alumina without prechloriding exposure.

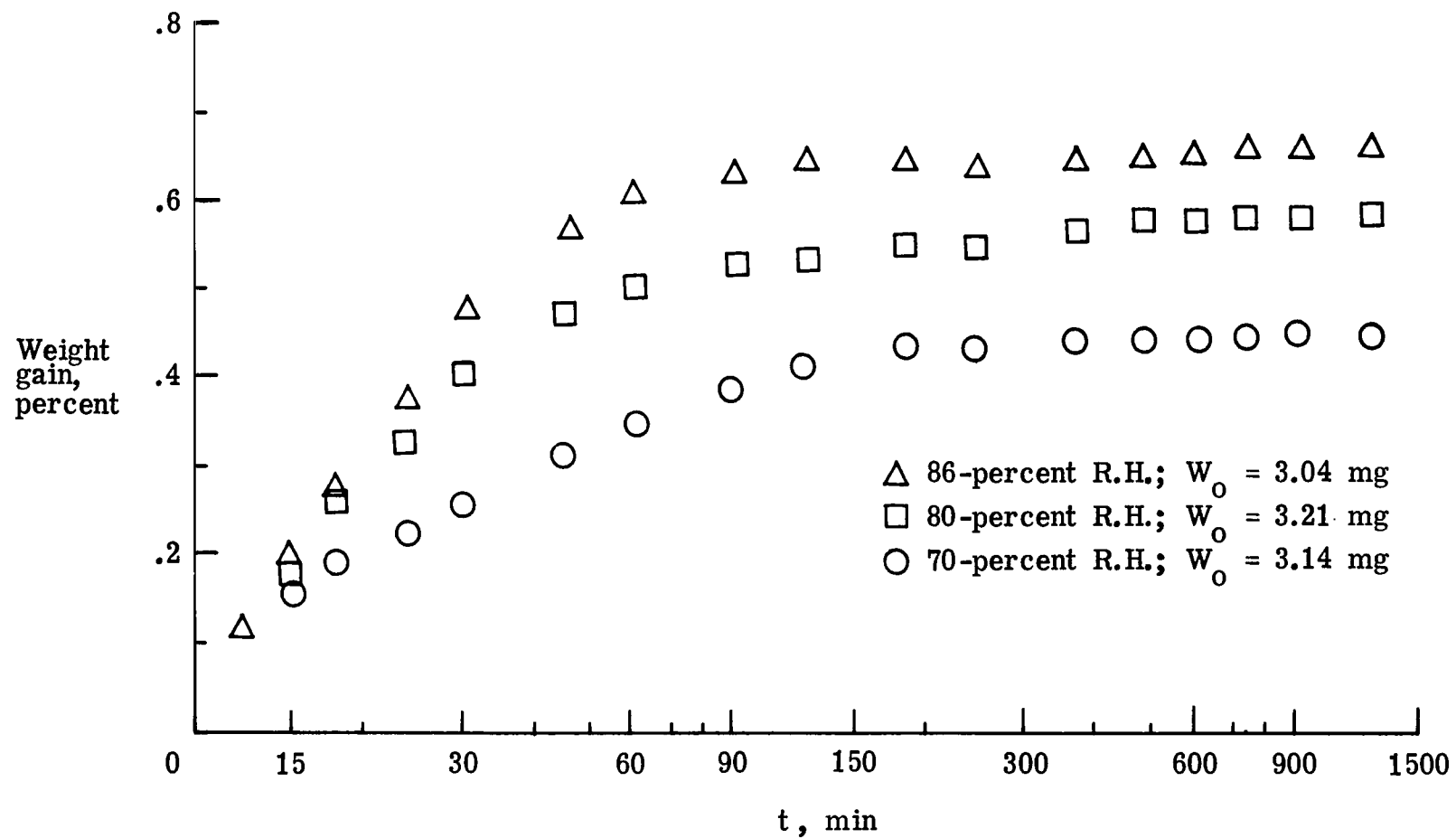


Figure 5.- Water sorption on samples of preparation 7 alumina without prechloriding exposure.

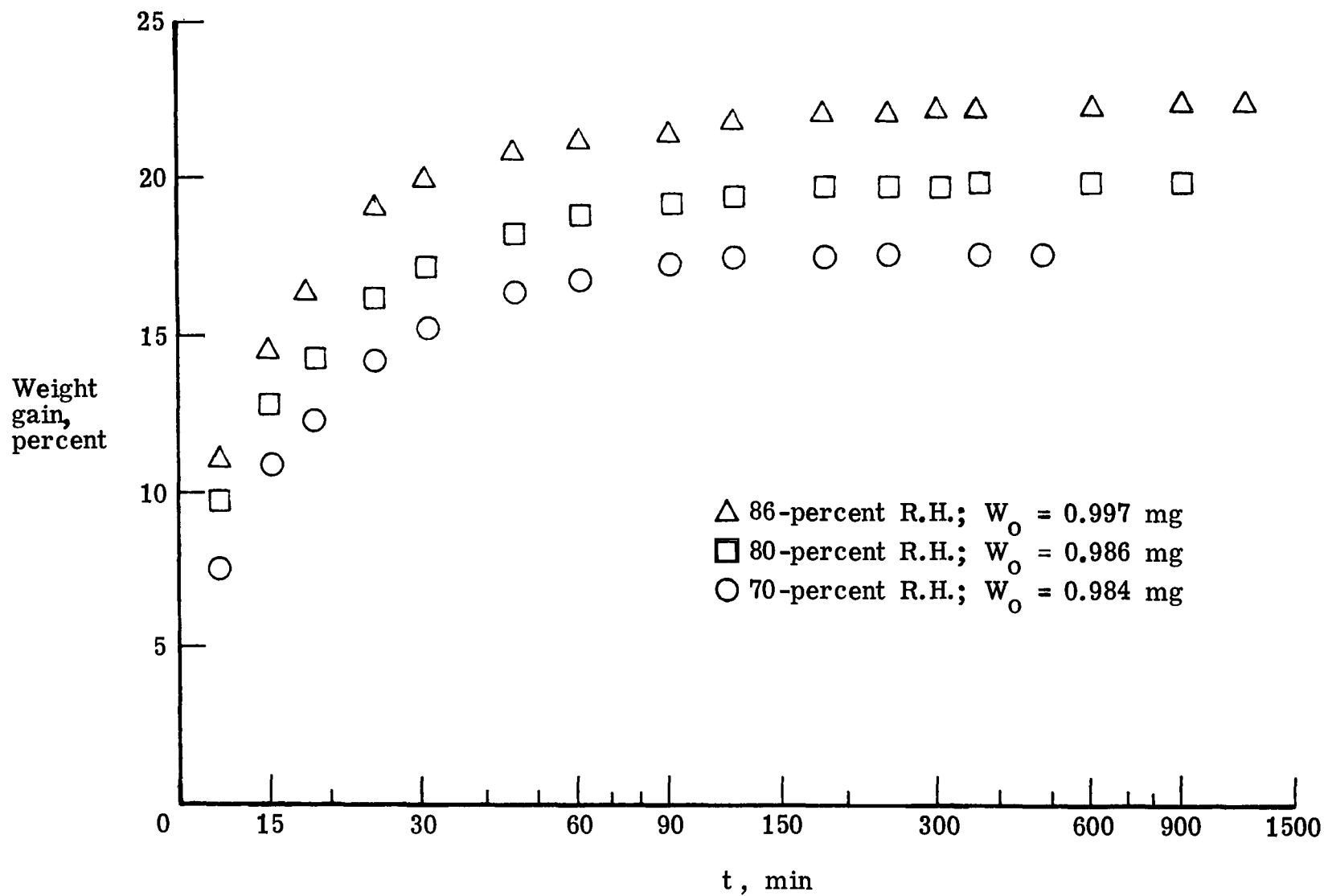


Figure 6.- Water sorption on samples of preparation 9 alumina without prechloriding exposure.

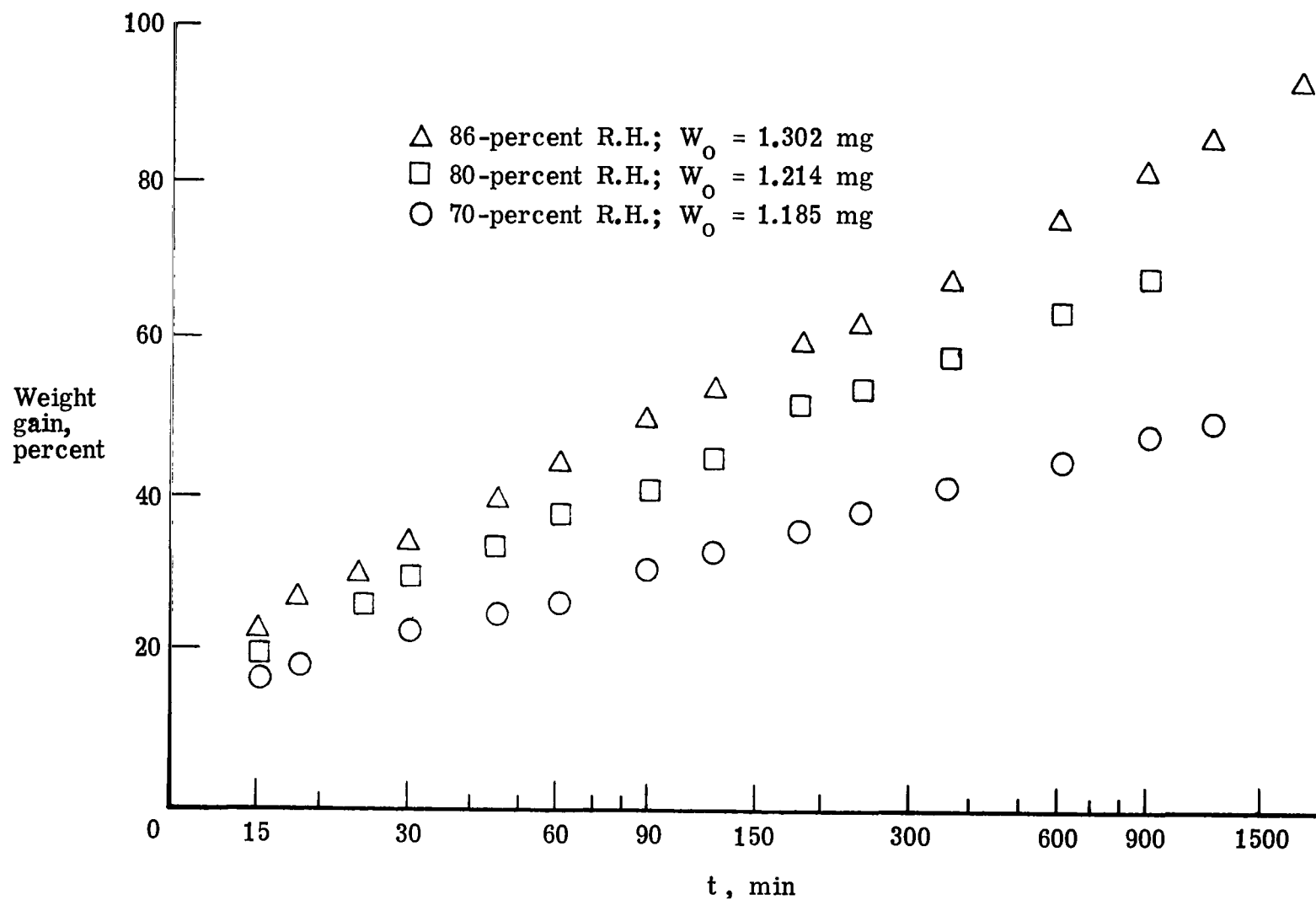


Figure 7.- Sorptions on fully chlorided preparation 9 alumina.

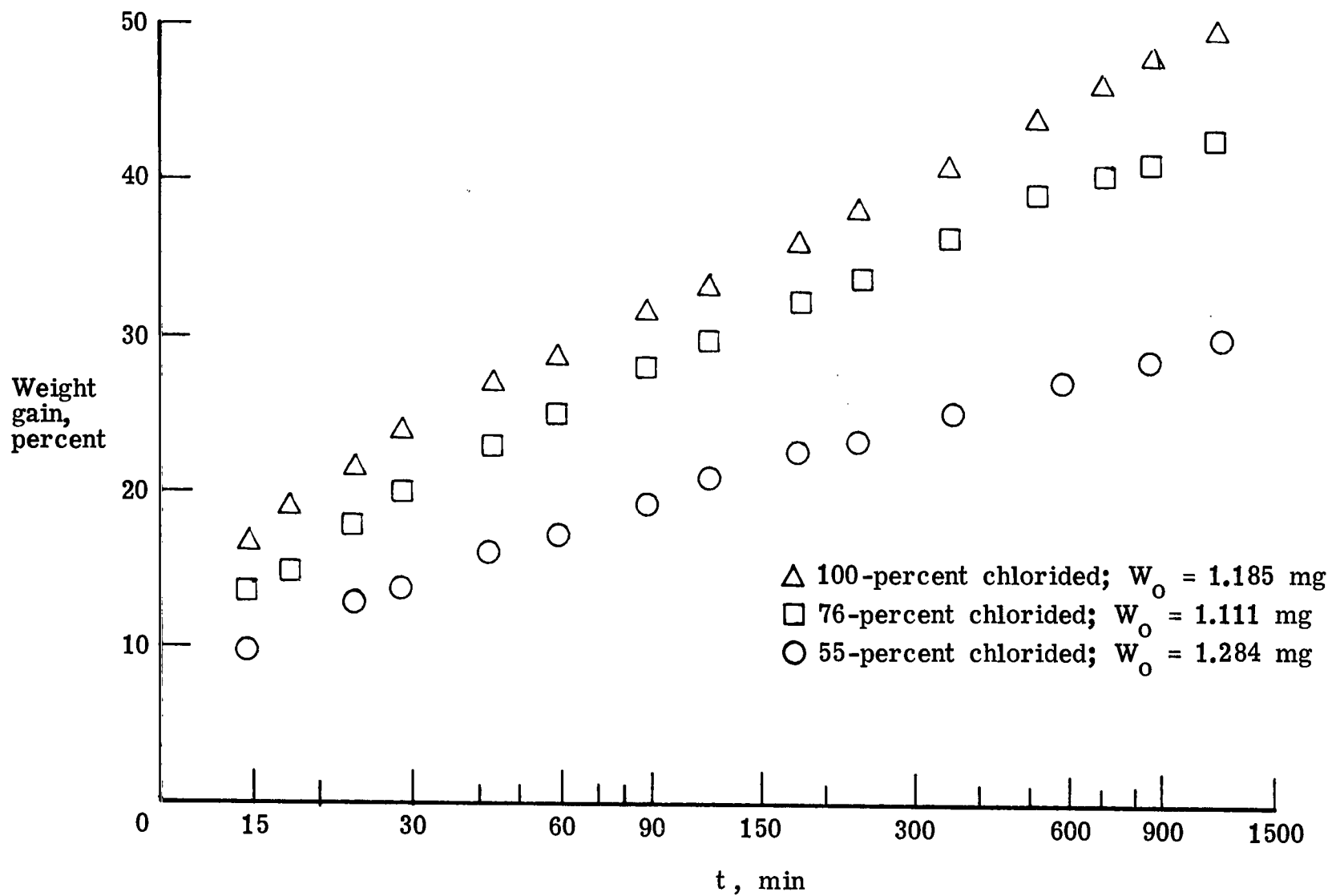


Figure 8.- Water sorptions on preparation 9 alumina at 70-percent relative humidity.

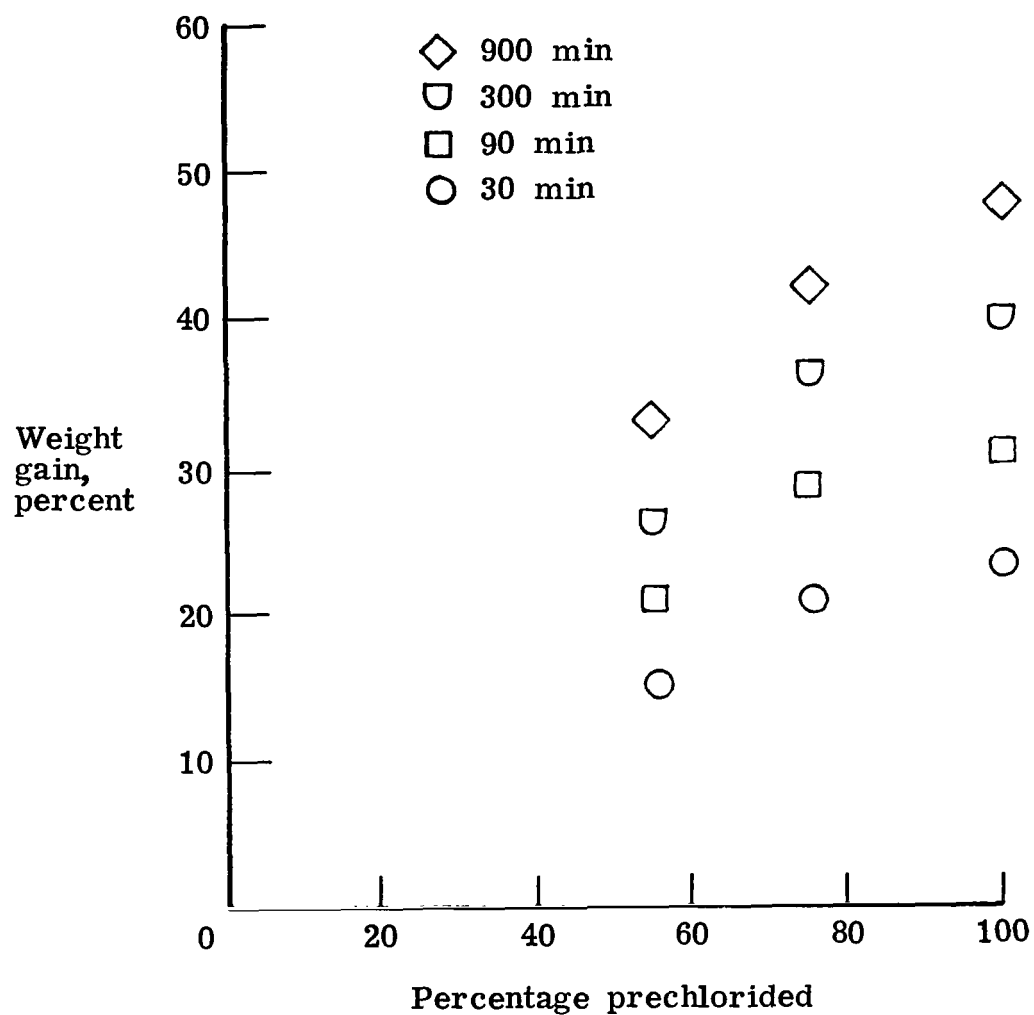


Figure 9.- Percentage weight gain for H₂O sorptions as a function of initial prechloriding coverage for selected times in sorption histories at 70-percent relative humidity on preparation 9 alumina.

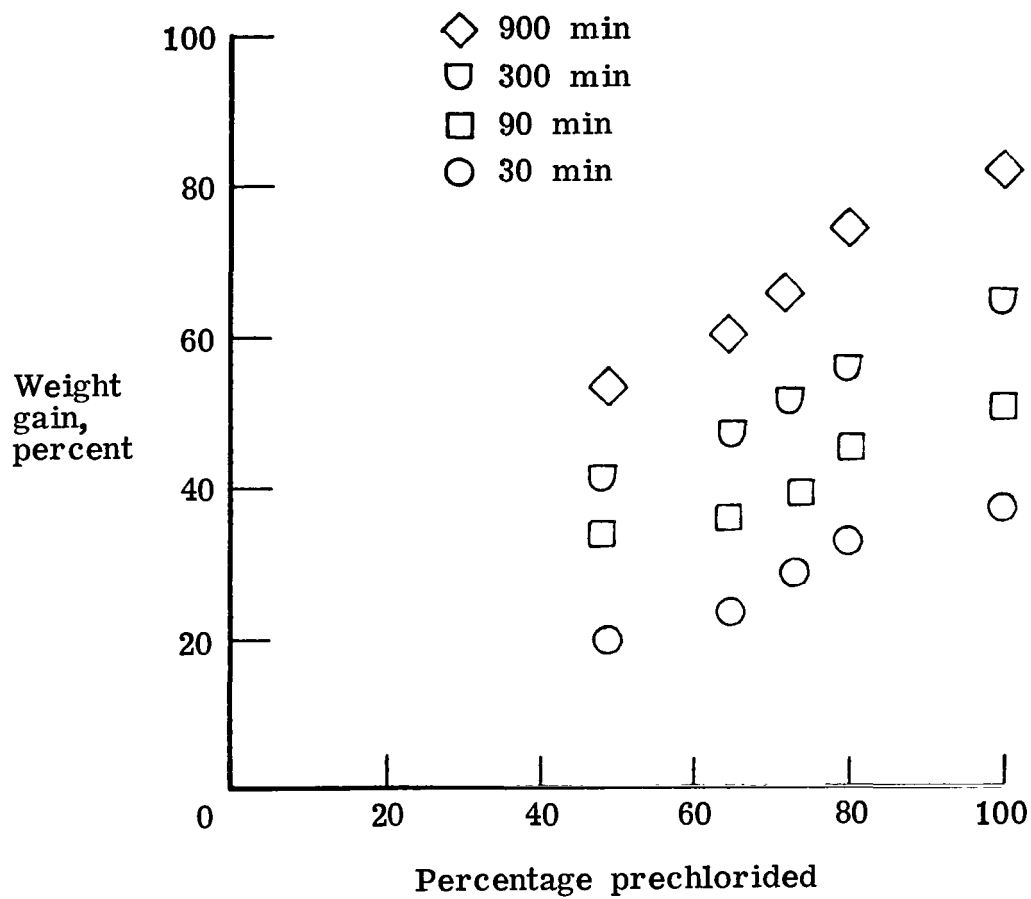


Figure 10.- Percentage weight gain for H_2O sorptions as a function of prechloriding coverage for selected times in sorption histories at 86-percent relative humidity on preparation 9 alumina.

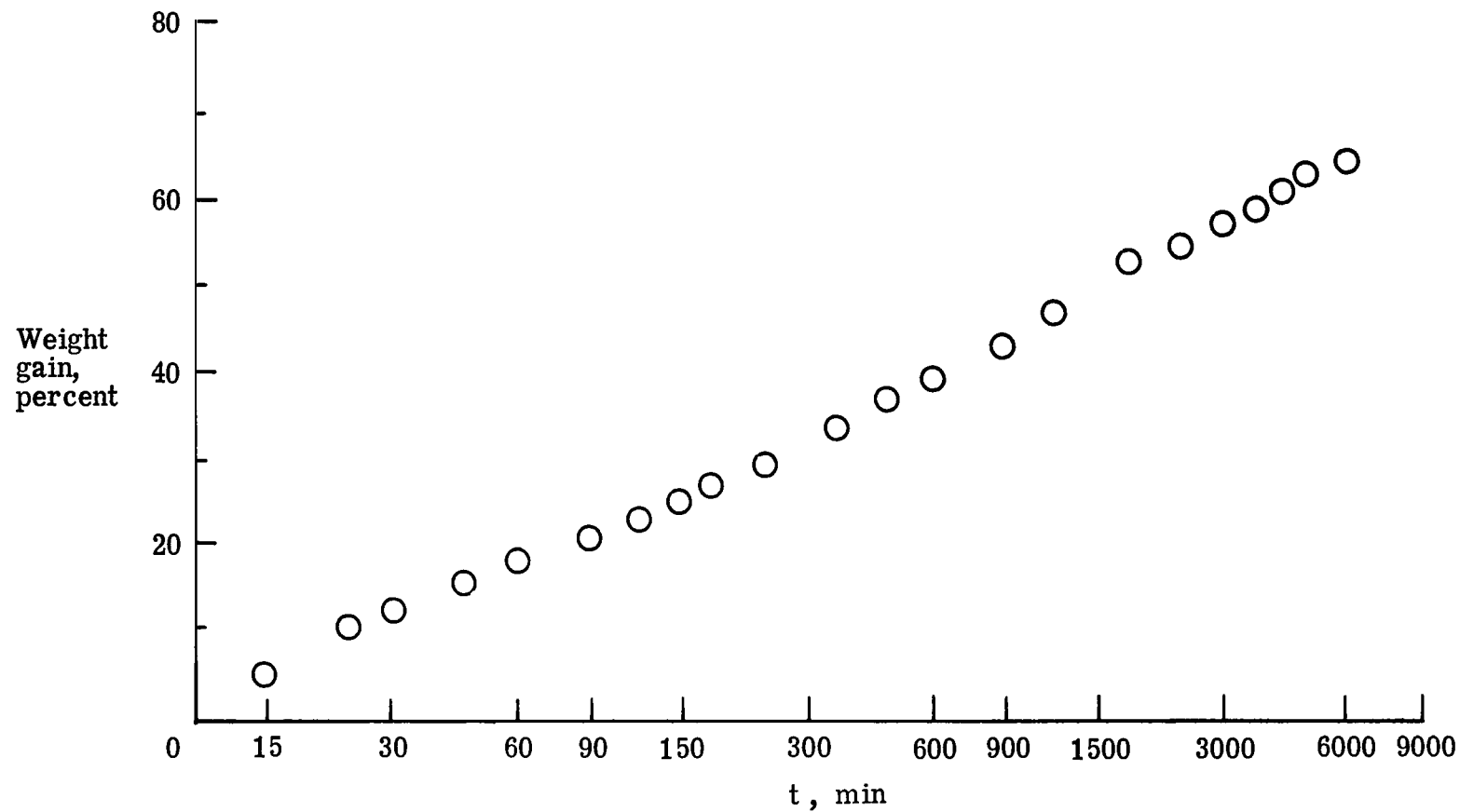


Figure 11.- Water sorption on fully chlorided preparation 6 alumina
at 86-percent relative humidity for $W_0 = 1.20$ mg.

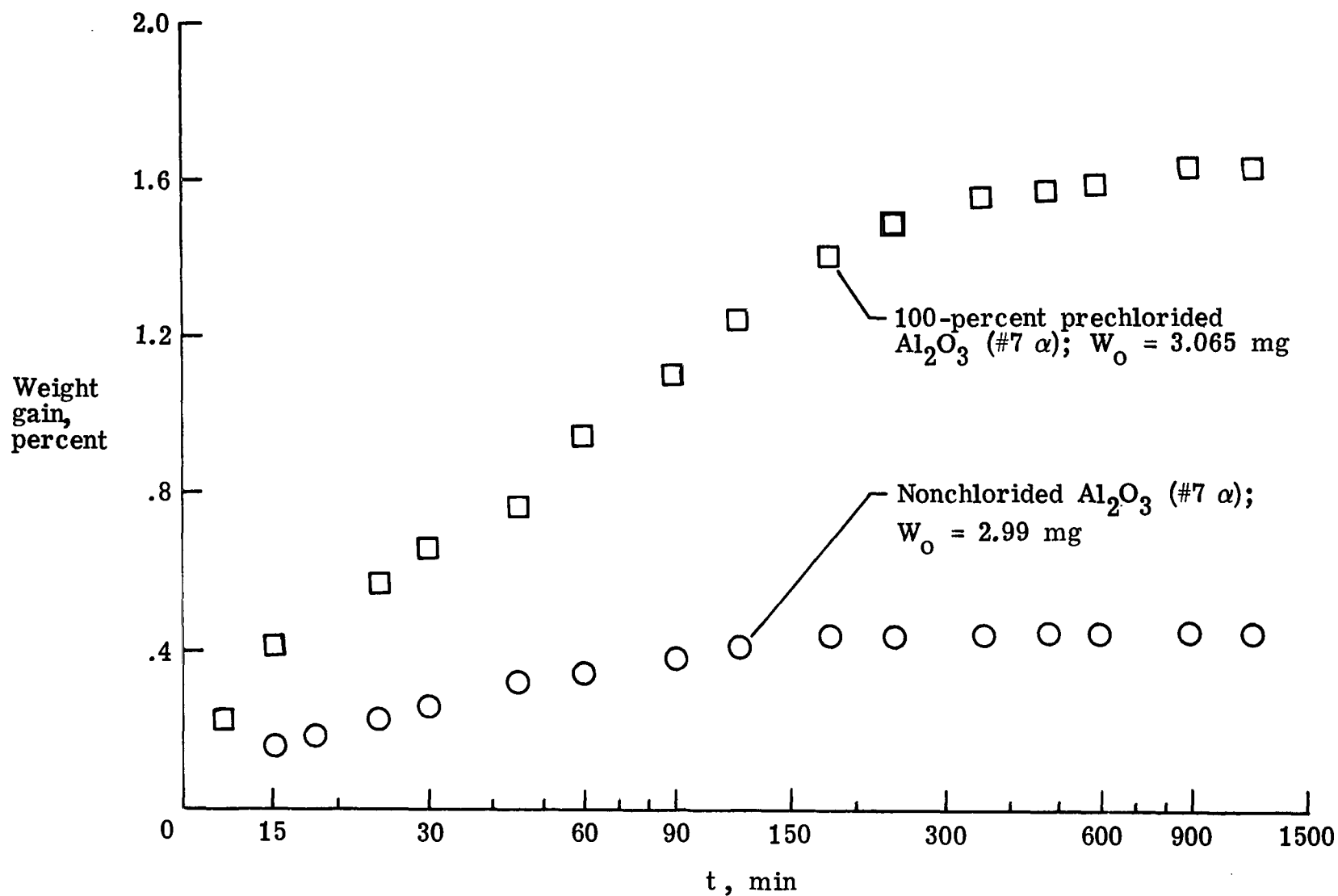


Figure 12.- Water sorption on preparation 7 alumina at 70-percent relative humidity.

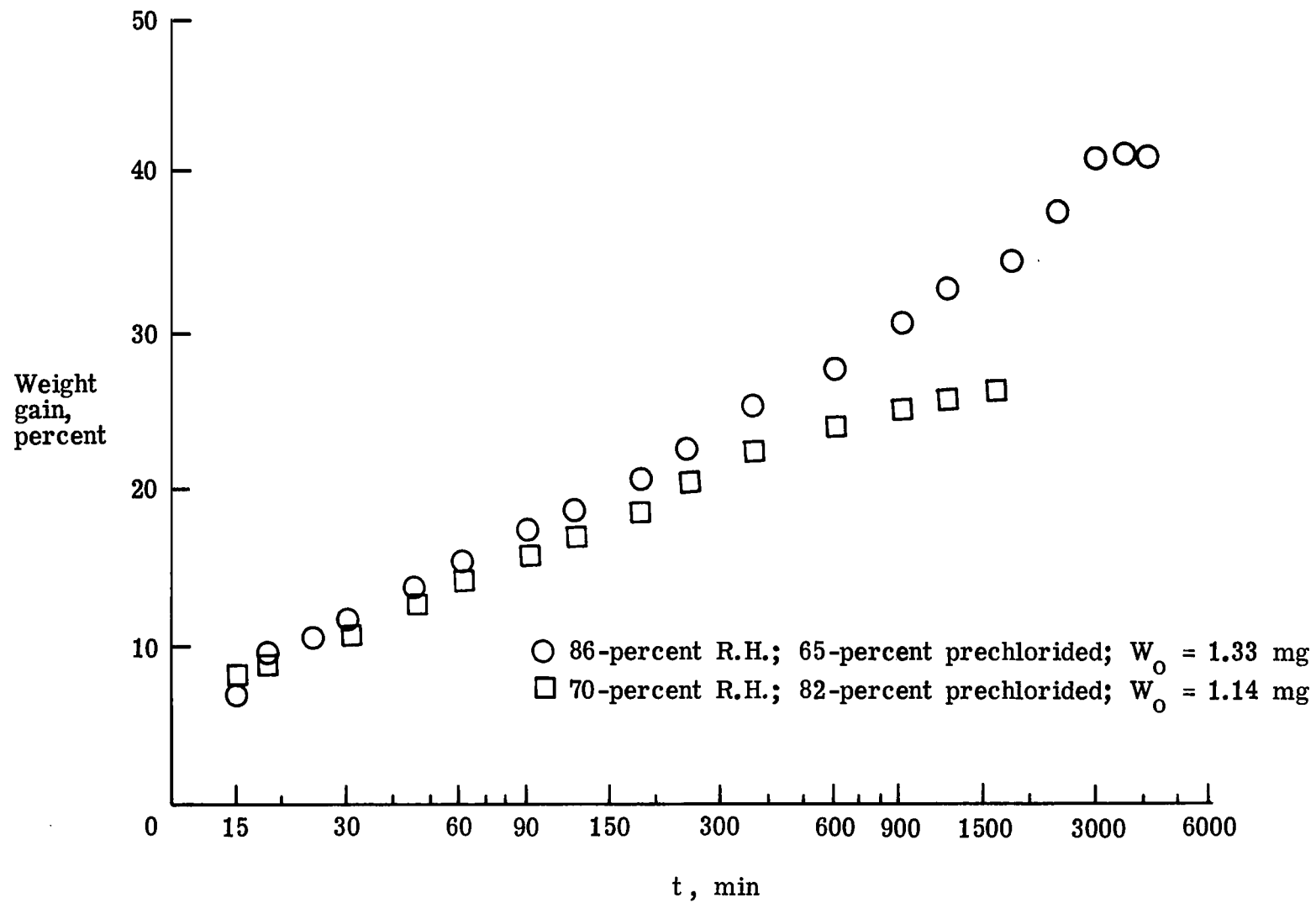


Figure 13.- Water sorptions on preparation 3 alumina.

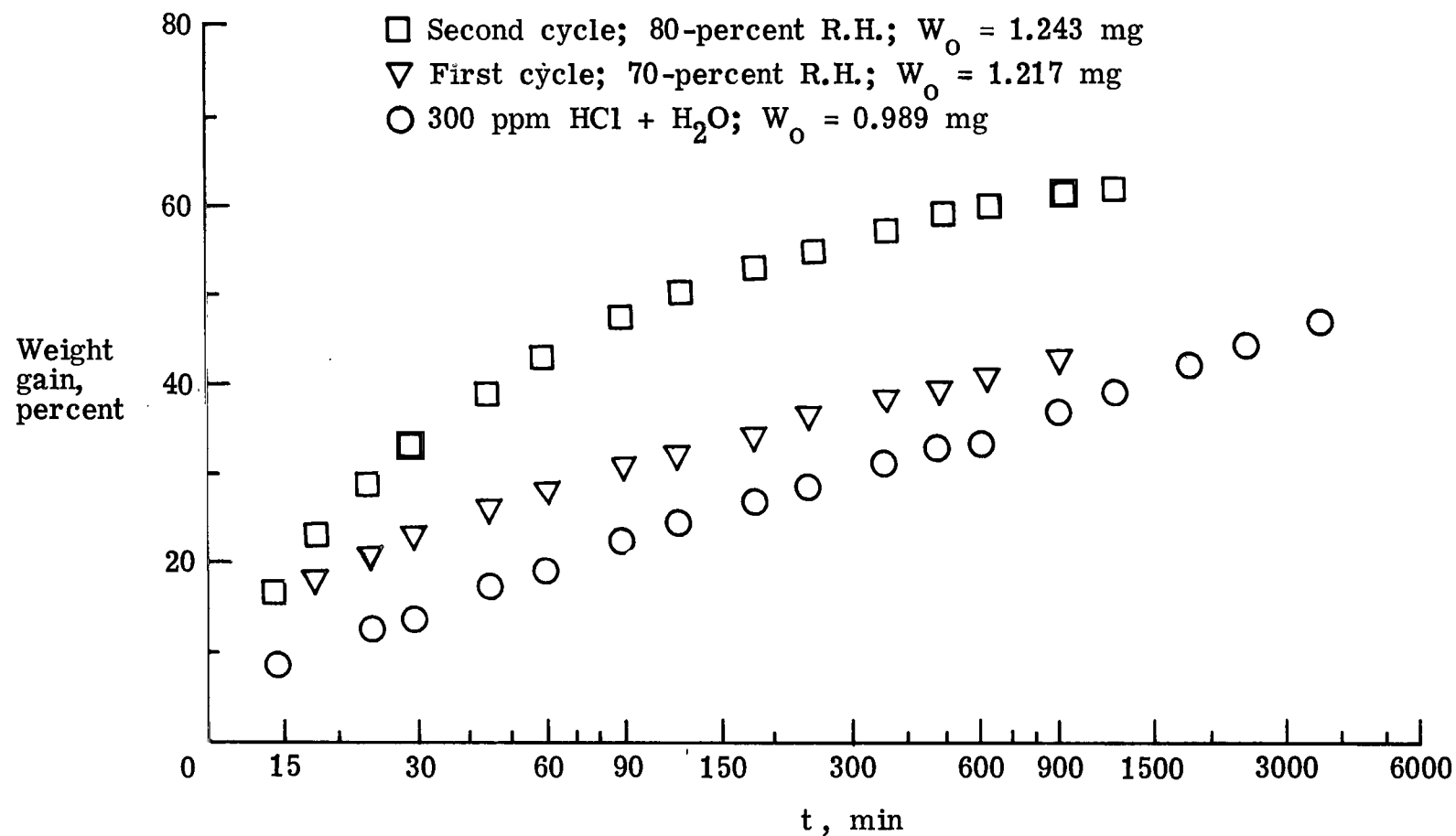


Figure 14.- HCl + H₂O prechloriding exposure followed by first and second water exposures on 92-percent prechlorided preparation 9 alumina.

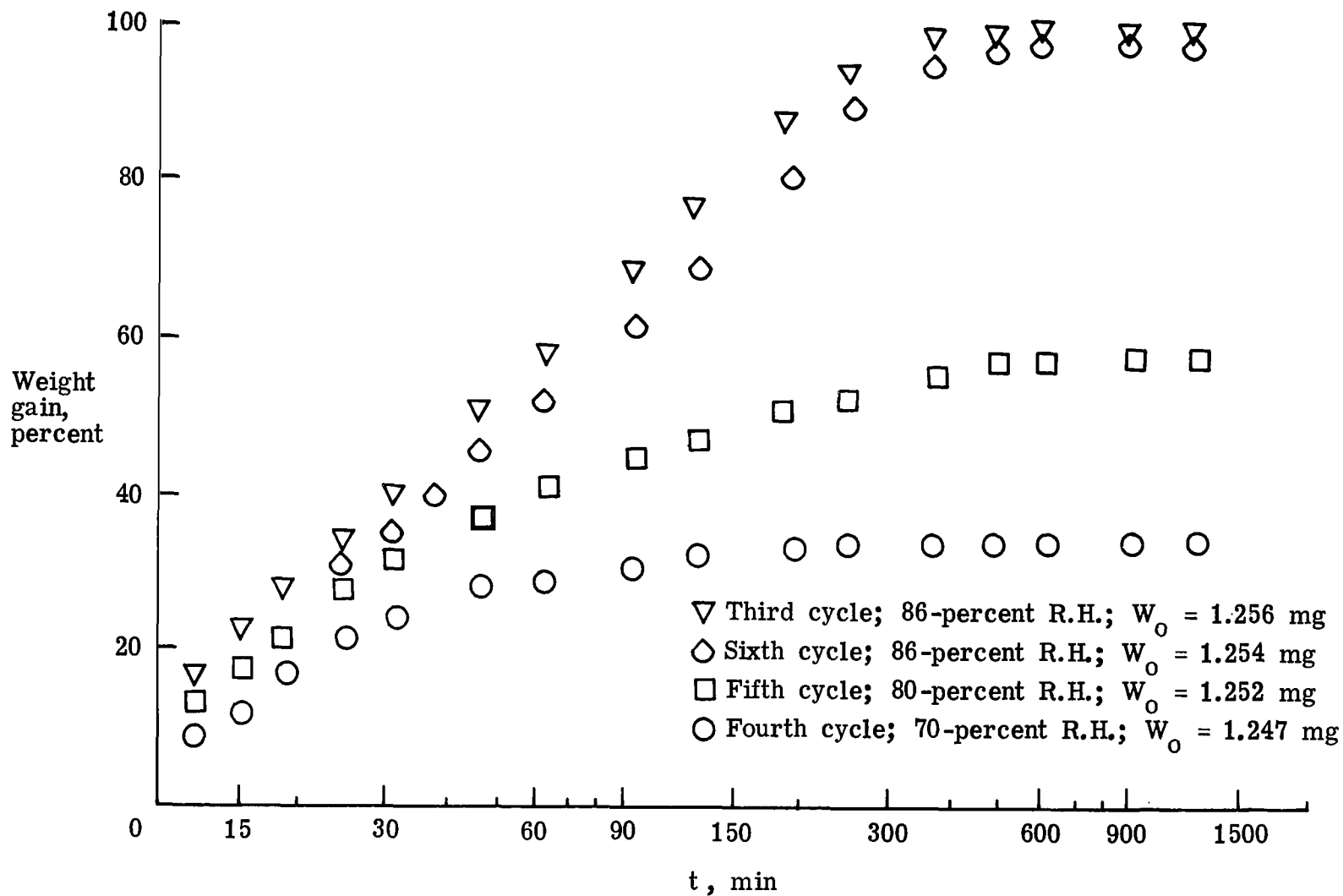


Figure 15.- Third, fourth, fifth, and sixth water cycles on 92-percent prechlorided preparation 9 alumina.

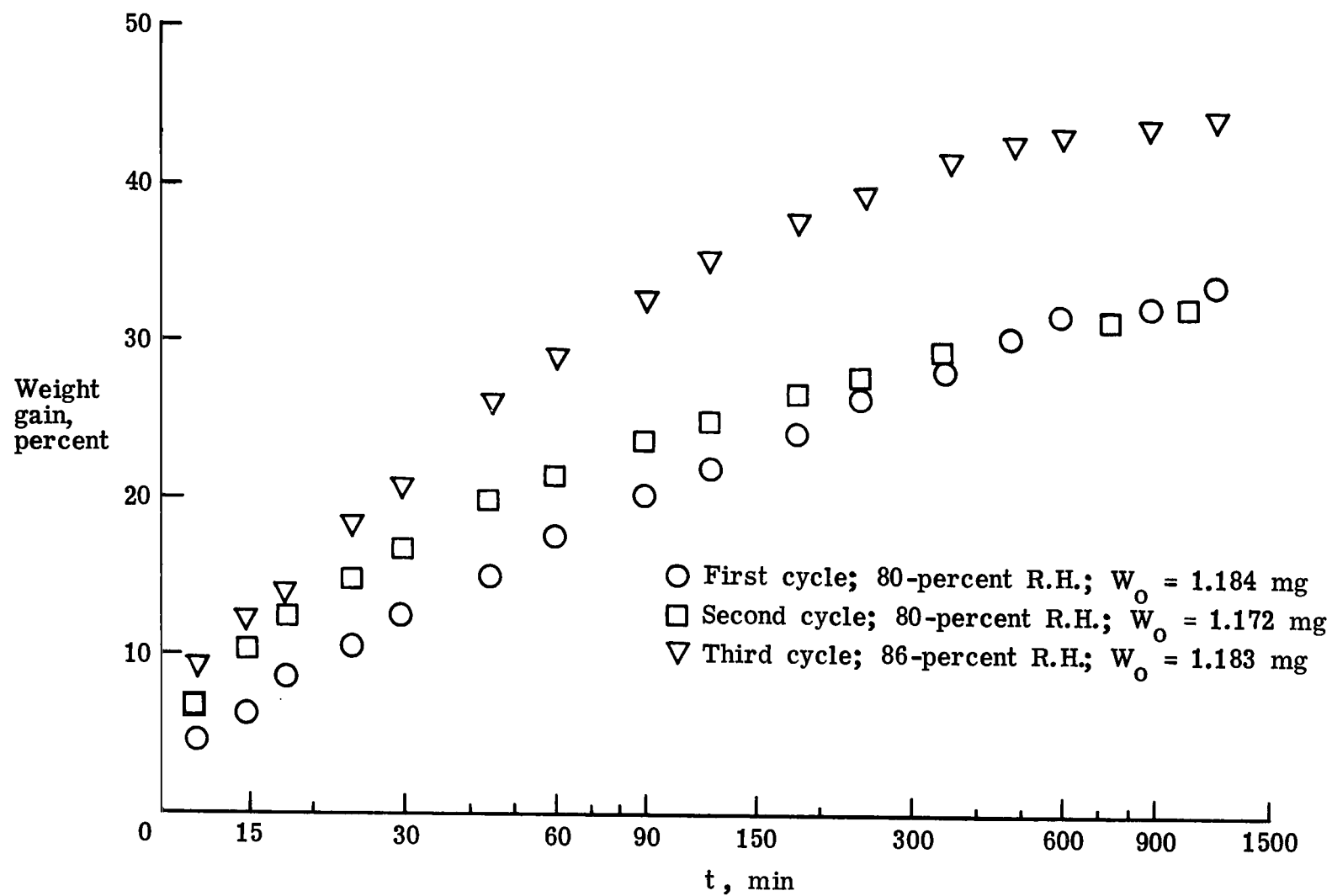


Figure 16.- First, second, and third water sorptions on fully chlorided preparation 3 alumina.

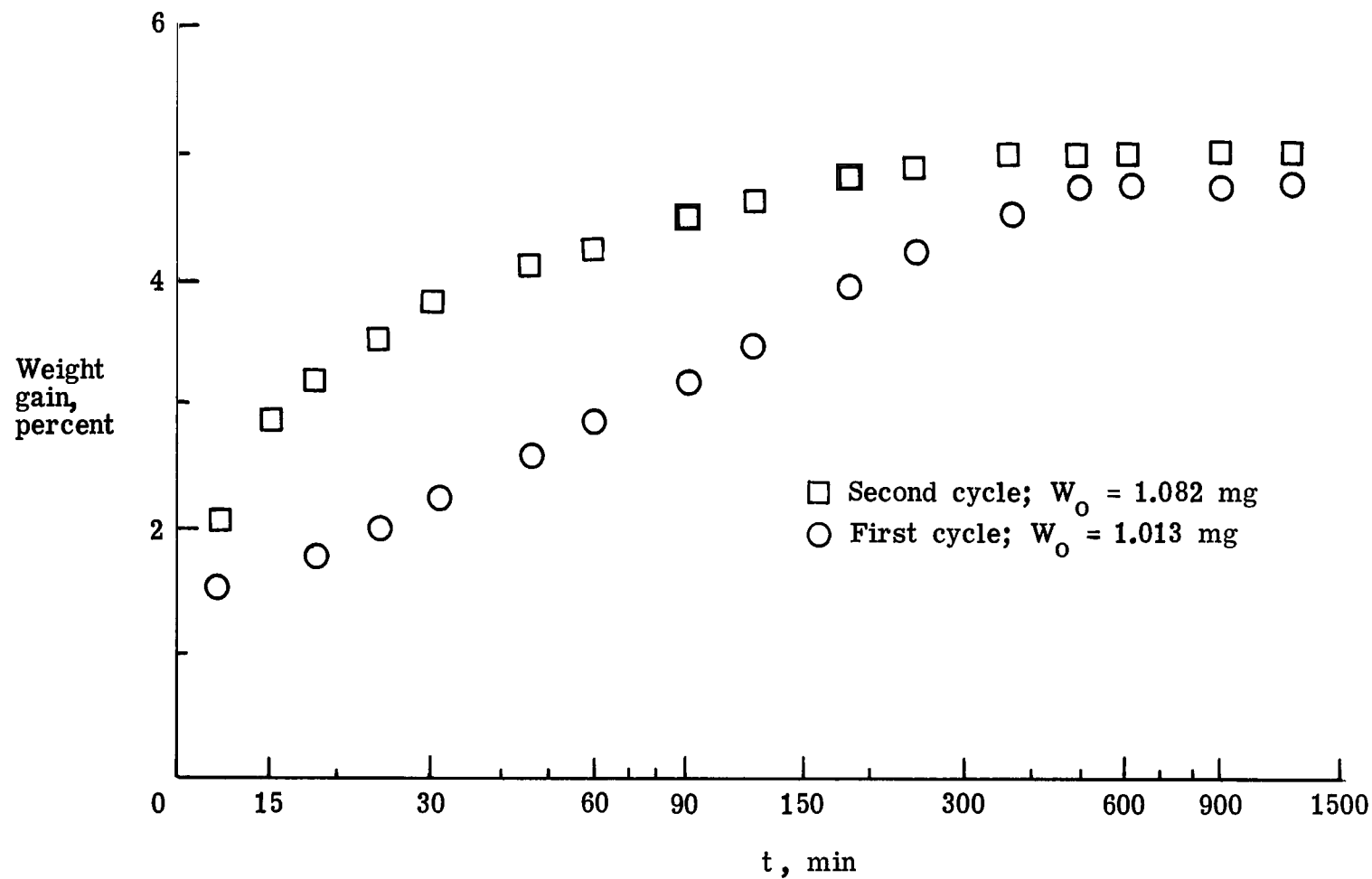


Figure 17.- First and second water exposure cycles on nonchlorided preparation 3 alumina at 70-percent relative humidity.

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